

Kinetics and mechanism of oxidative decolorization of azo dye acid orange 8 by sodium N-halo-p-toluenesulfonamides in acid medium: spectrophotometric approach

J.P. Shubha^{a*}, K. Vinutha^a, M. Dinamani^b, Puttaswamy^c

^aDepartment of Chemistry, Don Bosco Institute of Technology, Kumbalagodu, Mysore Road, Bangalore -560 074, India

^bDepartment of Chemistry, Dayananda Sagar College of Engineering, Kumaraswamy Layout, Bangalore – 560 078 India

^cDepartment of Chemistry, Central College Campus, Bangalore University, Bangalore - 560 001, India

Abstract: The kinetics of oxidative decolorization of acid orange 8 (AO8) by chloramine-T and bromamine-T in HClO₄ medium has been investigated spectrophotometrically ($\lambda_{max} = 490$ nm) at 298 K. Kinetic runs were executed under pretend first-order conditions of $[oxidant]_o \gg [AO8]_o$. Under identical experimental conditions, reactions with both the oxidants follow identical kinetics with a first-order dependence on each $[oxidant]_o$ and $[AO8]$ and a fractional-order dependence on $[HClO_4]$. Stoichiometry of the reaction was found to be 1:1 and the oxidation products were identified. The reaction was studied at dissimilar temperatures and activation parameters have been computed. Effects of p-toluenesulfonamide, halide ions, ionic strength and dielectric constant of the medium have been investigated. Reaction mixture fails to induce polymerization of acrylonitrile. The rate of oxidation of AO8 is about two-fold faster with BAT as compared to CAT. This may be endorsed to the diversity in electrophilicities of Cl⁺ and Br⁺ ions and also the van der Waal's radii of chlorine and bromine. Authentic mechanism and associated rate law have been deliberated for the observed kinetics.

Keywords: Azo dye, Acid Orange 8, Chloramine-T, Bromamine-T, Oxidation-Kinetics, Acid medium

I. Introduction

Color is the main petition of any textile. No issue how fabulous its constitution, if inaptly colored it is bound to be a fault as a commercial fabric. Fabrication and make use of replication dyes for structure dyeing has therefore become enormous production today. Simulation dyes have provided ubiquitous evolution of colorfast, extreme shades. However their venomous life has become a core of unsympathetic disquiet to environmentalists. Use of simulated dyes has an objectionable result on all forms of life. Existence of sulphur, naphthol, vat dyes, nitrates, acetic acid, soaps, enzymes chromium compounds and heavy metals and certain supplementary chemicals all cooperatively make the textile runoff exceptionally noxious. Other injurious chemicals present in the water may be formaldehyde based dye fixing agents, chlorinated stain removers, hydrocarbon based softeners, non bio degradable dyeing chemicals.

Discharge containing azo dyes by dye, textile and food processing industries origin key environmental tribulations and reduction of toxicity caused by these dyes is a chief concern in waste water handling. Acid orange 8 is one of the harmful dye effluents from textile industries and removal of this dye by simple, cost effective method is most required for healthy public. Azo dyes contain one or more azo groups (-N=N-) as the primary chromophore and they form the largest class of synthetic dyes. There are several monoazo dyes which are widely used as colorants in common foods and drugs [1]. The discharge of highly colored synthetic dye effluents can be very damaging to the receiving water bodies, since these dyes in water strongly absorb sunlight, which decreases the intensity of light absorbed by water plants and phytoplankton, reducing photosynthesis and the oxygenation of water reservoirs [2]. Also, public perception of water quality is greatly influenced by its color. The presence of unnatural colors is esthetically unpleasant and tends to be associated with contamination [3]. In addition, dyes used in the textile industry may be toxic to aquatic organisms and can be resistant to natural biological degradation [2,4,5]. Effluents containing azo dyes discharged by food and dye industries, cause significant environmental problems. Hence, removal of azo dye effluents generated by food and dye industries is a main issue in waste water treatment. These effluents are commonly treated using physico-chemical methods such as adsorption, photodegradation and coagulation. All of these processes are very expensive and not so simple. Therefore, there is a need for inexpensive and simple methods to abolish harmful dyes in effluents. The oxidation of azo dyes has attracted much attention in recent years [6-11].

Acid orange 8 (AO8) is used in textile dyeing [1]. An extensive literature survey reveals that there are no reports on the oxidation of AO8 by any oxidants from the standpoint of the kinetic and mechanistic approach.

Hence, it was felt desirable to examine the oxidative decolorization of AO8 with N-haloamines to explore the kinetic and mechanistic aspects of its redox chemistry.

The most important aim of this work was to promote the decolorization of AO8 by N-haloamine, has a low energy cost and is economical. The effectiveness of the proposed process was evaluated by its capability to promote decreases in color and total organic carbon content. The high efficiency observed with the dye model showed that this economic, easily operated and maintained treatment process could also be employed in the remediation of effluents.

The sodium salts of arylhalosulfonamides generally known as organic haloamines have attracted the attention of chemists, as versatile redox titrants [12]. The miscellaneous chemical behaviour of organic haloamines is accredited in general to their ability to act as halonium cations, hypohalites, N-anions which act both as bases and nucleophiles and nitrenoids in limiting cases [13]. As a consequence, these compounds react with a wide range of functional groups and influence a variety of molecular changes. Organic haloamines are mild oxidants containing a strongly polarized N-linked halogen which is in +1 state. The subject has been broadly reviewed and well studied [13-17]. The important chlorine compound of this class is sodium N-chloro-p-toluenesulfonamide or chloramine-T (CAT), is a byproduct in the manufacture of saccharin. This reagent has been exploited as an oxidant for a variety of substrates in both acidic and alkaline media¹⁻¹¹. The bromine analogue of CAT, bromamine-T (BAT) is gaining importance as a mild oxidant and is found to be a better oxidizing agent than the chloro derivative [14-16, 23-25]. This reagent can be easily prepared by the bromination of CAT. Although BAT is a better oxidant compare to CAT, an extensive literature survey reveals that only sporadic references are available about the oxidative behaviour of BAT from the kinetic and mechanistic points of view. This aroused our interest to carry out the detailed kinetic study on the oxidation of diclofenac by the closely related reagents CAT and BAT in alkaline medium to explore the mechanistic aspects of these oxidations and also to assess their relative rates. The studies extended to the relevant kinetic features of CAT and BAT and to identify the reactive oxidizing species of these oxidants in aqueous alkaline medium.

In the light of existing information and in continuation of our research interest on the kinetic and mechanistic investigations of oxidation of various substrates in general and dyes in particular by CAT and BAT, the title reaction was undertaken. Accordingly, in this communication we report on the comprehensive kinetics of AO8 oxidation by CAT and BAT in HClO₄ medium at 298 K.

II. Experimental

Materials

Chloramine-T (E. Merck) was purified by the method of Morris et al [26]. Bromamine-T was obtained [27] by the partial debromination of dibromamine-T (DBT) by 4 mol dm⁻³ NaOH. The purity of these reagents was assayed iodometrically to determine the active halogen content. Aqueous solution of these oxidants was standardized by the iodometric method and stored in brown bottles to prevent any of its photochemical deterioration. C.I. Acid orange 8 (S.d. fine-chem Ltd.) was of acceptable grade of purity and was used as received. Solvent isotope studies were made with D₂O (99.4 %) supplied by BARC, Mumbai, India. Analytical grade chemicals and double distilled water was used throughout. The regression coefficient (r) was calculated using f_x – 350TL scientific calculator.

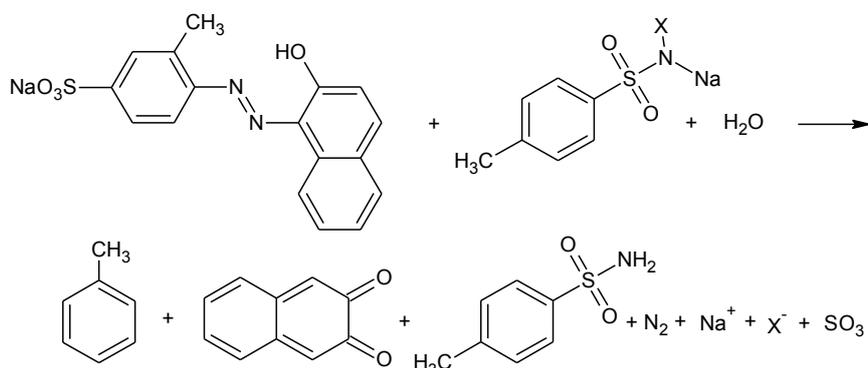
Kinetic measurements

The kinetic runs were performed under pseudo first-order conditions with a known excess of the [oxidant]₀ over [AO8]₀ at 298 K using a UV-visible spectrophotometer (Digital Spectrophotometer 166, Systronics, India). In the present study, the kinetic experiments were carried out between 288 and 313 K. For this purpose, a Raaga Ultra Cold Chamber with digital temperature control (India) was used. A constant temperature was maintained with an accuracy of ± 0.1 °C. Reactions were carried out in glass stoppered Pyrex boiling tubes whose outer surfaces were coated black to eliminate any photochemical effects. The oxidant as well as requisite amounts of dye and HClO₄ solutions and water (to keep the total volume constant for all runs) taken in separate tubes were thermostatted for 30 min at 298 K. The reaction was initiated by the rapid addition of a measured amount of oxidant to the stirred reaction mixture. Immediately, the solution was pipetted into a cuvette placed in the spectrophotometer. Absorbance measurements were made at 490 nm (λ_{\max} of AO8) for nearly three half lives. The absorbance readings at t = 0 and t = t are D₀ and D_t. Plots log D₀/D_t versus time were made to evaluate the pseudo-first-order rate constants (k') which found reproducible within ± 4-5%. Regression analysis of the experimental data was carried out on an fx – 100W scientific calculator to evaluate the regression coefficient, r.

Reaction stoichiometry

Reaction mixtures containing different ratios of oxidant to AO8 in presence of 2.0 x 10⁻³ mol dm⁻³ HClO₄ were equilibrated at 298 K for 24 h. The unreacted oxidant in the reaction mixture was determined by

iodometric titration. This analysis showed that in both the cases one mole of AO8 consumed one mole of oxidant and the observed reaction stoichiometry is represented as:



Product analysis

In the stoichiometric proportion, the reaction mixtures containing different concentrations of oxidant and substrate in $2.0 \times 10^{-3} \text{ mol dm}^{-4} \text{ HClO}_4$ under stirred condition was allowed to react for 24 h at 298 K. After completion of the reaction (monitored by thin layer chromatography), the reaction products were neutralized with alkali and extracted with ether. The organic products were subjected to spot tests and chromatographic analysis, which revealed the formation of toluene and naphthaquinone as the oxidation products of AO8 and p-toluenesulfonamide as the reduction product of the oxidant. The products were confirmed by Mass spectral analysis (Fig. 1, Fig. 2).

p-toluenesulfonamide was extracted with ethyl acetate and detected by paper chromatography. Benzyl alcohol saturated with water was used as the solvent system with 0.5 % vanillin in 1 % HCl solution in ethanol as spray reagent ($R_f = 0.905$). Further, the molecular ion peak of 171 amu (Fig. 3) confirms p-toluenesulfonamide. All other peaks observed in GC-MS can be interpreted in accordance with the observed structure.

III. Results and Discussion

Effect of reactant concentration on the rate

The kinetics of oxidation of AO8 by CAT and BAT (hereafter abridged as oxidant) have been investigated at several initial concentrations of the reactants, under pseudo first-order conditions of $[\text{oxidant}]_0 \gg [\text{substrate}]_0$, in presence of HClO_4 at 298 K in both cases. The kinetic and mechanistic features for the oxidation of AO8 with the closely related compounds CAB and BAB in HClO_4 medium are same under identical experimental conditions but the comparative rates of oxidation of AO8 by BAT are about two-fold faster than CAT.

Under the conditions $[\text{oxidant}]_0 \gg [\text{AO8}]_0$ at constant $[\text{oxidant}]_0$, $[\text{HClO}_4]$, temperature, plots of log (absorbance) versus time were linear ($r > 0.9952$) indicating a first-order dependence of rate on $[\text{AO8}]_0$ in both the cases. The linearity of these plots in both cases, together with the constancy of the slopes obtained at different $[\text{AO8}]_0$, substantiates the first-order dependence of rate on $[\text{AO8}]_0$. The pseudo first-order rate constants (k') obtained are recorded in Table 1. Under the same experimental conditions the rate of reaction increased in $[\text{oxidant}]_0$ (Table 1) and plots of log k' versus log $[\text{oxidant}]_0$ were linear ($r > 0.9955$) with unit slopes in both the cases. This establishes that the order of the reaction is first-order with respect to $[\text{oxidant}]_0$. Further, plots of k' versus $[\text{oxidant}]_0$ were linear ($r > 0.9980$) passing through the origin corroborate the first-order dependence on $[\text{oxidant}]_0$.

The rate of reaction augmented with increase in $[\text{HClO}_4]$ (Table 1) and plots of log k' versus log $[\text{HClO}_4]$ were linear ($r > 0.982$) with slopes of 0.69 and 0.66 for CAT and BAT, showing a fractional-order dependence on $[\text{HClO}_4]$.

Effects of halide ions and p-toluenesulfonamide concentration on the rate

Addition of halide ions, Cl^- or Br^- , in the form of their sodium salts ($1.0 \times 10^{-3} - 8.0 \times 10^{-3} \text{ mol dm}^{-3}$) showed no pronounced effect on the rate. This indicates that the halide ions play no role in the reaction. The ionic strength of the reaction medium was varied from 0.1 to 0.3 mol dm^{-3} with NaClO_4 solution keeping other experimental conditions constant. It was found that addition of NaClO_4 showed negligible effect on the reaction rate, representing the participation of nonionic species in the rate-determining step. Hence no attempts were made to maintain the ionic strength of the medium stable for kinetic runs. Addition of p-toluenesulfonamide

(RNH₂) to the reaction mixture (5.0 x 10⁻³ mol dm⁻³) did not influence the rate significantly indicates that RNH₂ is not involved in any step prior to the rate determining step of the proposed scheme.

Effect of dielectric constant of the medium on the rate

The dielectric constant (D) of the medium was mottled by adding MeOH (0-30 % v/v) to the reaction mixture with all other experimental conditions being held constant. The rates were found to be increased with both the oxidants.

Effect of solvent isotope on the rate

Since the oxidation of AO8 by CAT and BAT was increased with H⁺ ions, the solvent isotope effect was studied in D₂O as the solvent medium for both the oxidants. The rate constants for CAT and BAT revealed that k' (H₂O) was equal to 3.26 x 10⁻⁴ s⁻¹ and 9.80 x 10⁻⁴ s⁻¹, and k' (D₂O) was 3.75 x 10⁻⁴ s⁻¹ and 12.7 x 10⁻⁴ s⁻¹, respectively. Thus, the solvent isotope effect, k' (H₂O) / k' (D₂O) were found to be 0.86 and 0.77 for CAT and BAT.

Effect of temperature on the rate

The reaction was studied at different temperatures (288-313 K), keeping other experimental conditions constant. From Arrhenius plots of log k' vs. 1/T (r > 0.9955), composite activation parameters (E_a, ΔH[‡], ΔS[‡], ΔG[‡] and log A) were computed for the oxidation of AO8 by CAT and BAT. These data are summarized in Table 2.

Test for free radicals

Alkene monomers such as acrylonitrile and freshly prepared 10% acrylamide solutions were added to the reaction mixture to instigate polymerization by free radicals formed in situ. The lack of polymerization indicated the absence of free radicals in the reaction mixture. This clearly ruled out the possibility of free radical mechanism. The controlled experiments were also performed under similar reaction conditions without oxidant.

Reactive species of sodium N-halo-p-toluenesulfonamides

Organic N-haloamines are sources of positive halogens and these reagents have been exploited as oxidant for a variety of substrates in both acidic and alkaline media [12, 16]. Since organic N-haloamines have analogous chemical properties, it is predicted that identical equilibria exist in aqueous acidic and basic solutions of these compounds [25-26]. Chloramine-T and bromamine-T act as oxidizing agents in acidic and alkaline media [27-29] with a two electron change per mole giving p-toluenesulfonamide (PTS) and NaCl or NaBr. The redox potential of CAT-PTS couple is pH dependent [25] and decreases with increase in pH of the medium (E_{redox} 1.138 V, 1.778 V, 0.614 V and 0.5 V at pH 0.65, 7.0, 9.7 and 12, respectively). In view of the homogeneity in properties of N-haloamines, similar redox potential behaviour can be expected and BAT also. The nature of the active oxidizing species and mechanism depends on the nature of halogen atom, the groups attached to the nitrogen and the reaction condition. The species accountable for such oxidizing character may be different depending on the pH of the medium.

Chloramine-T and bromamine-T (TsNXNa) are moderately strong electrolytes [26] in aqueous solutions (TsNXNa \rightleftharpoons TsNX + Na⁺), and depending on the pH of the medium, these reagents furnish different types of reactive species in solutions [26, 28-29]. The possible oxidizing species present in acid medium are TsNHX, TsNX₂, HOX and also perhaps H₂OX⁺.

Reaction scheme

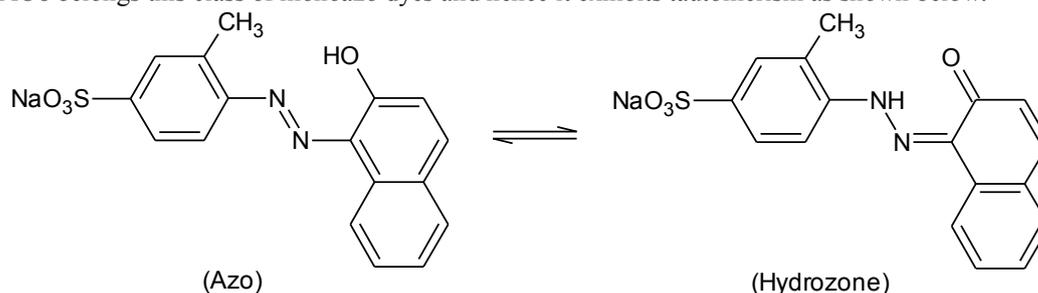
In the present studies, the first-order dependence of rate on [oxidant]₀ and no effect of rate on [TsNH₂] clearly ruled out the opportunity of both TsNX₂ and HOX as reactive species. The probability of the dichloro compound as the reactive species is ruled out, since clear first-order plots are obtained for the desertion of the [substrate]. Added p-toluenesulfonamide does not hinder the reaction indicating that HOX is not principally involved in the rate determining step. Further, Bishop and Jennings [28] have shown in their studies on aqueous solutions of CAT, that pH~ 3-4, the concentration of anion TsN⁻Cl is greater than that of the free acid.



Hence a protonation equilibrium (1) suggesting the anion can be assumed as the reactive oxidizing species. Since organic haloamines have similar chemical properties, the same equilibrium can be expected for BAT also.



Scheme 2. A general reaction scheme for the oxidation of AO8 by CAT and BAT in acid medium. In general azo dyes containing hydroxyl groups conjugated to azo group exhibit azo-hydrazone tautomerism. Since AO8 belongs to this class of monoazo dyes and hence it exhibits tautomerism as shown below.



In the present case, the azo form of the dye reacts with the conjugate acid of the oxidant to form AO8-oxidant complex (X) with the elimination of RNH_2 . The complex in acid medium undergoes protodesulfonation followed by hydrolysis and cleavage of azo bond to yield the ultimate products toluene and 1,2-naphthaquinone as shown in scheme 2.

Kinetic rate law

A detailed mode of oxidation of AO8 by CAT and BAT in acid medium is illustrated in Scheme 2, where the structure of the transitional complex X is shown. In a fast initial equilibrium (step (i) of Scheme 1), the anion RNX^- , in acid accelerating step generates the active oxidizing species RNHX . In a slow / rate limiting step (step (ii)), the lone pair of electrons on oxygen of AO8 attacks the positive halogen of RNHX forming an intermediate species X. This intermediate complex X (step (iii)) undergoes hydrolysis followed by several fast steps leading to the formation of naphthaquinone and naphthalene as end products.

If $[\text{oxidant}]_t$ represents the total concentration of the oxidant, then from steps (i) and (ii) of Scheme 1,

$$[\text{oxidant}]_t = [\text{RNX}^-] + [\text{RNHX}] \quad (9)$$

By substituting $[\text{RNX}^-]$ from step (i) of Scheme 1, into Eqn 9 and solving for $[\text{RNHX}]$, one gets,

$$[\text{RNHX}] = \frac{K_1 [\text{oxidant}]_t [\text{H}^+]}{1 + K_1 [\text{H}^+]} \quad (10)$$

From the slow and rate determining step (step (ii) of Scheme 1),

$$\text{Rate} = k_2 [\text{RNHX}] [\text{AO8}] \quad (11)$$

By substituting for $[\text{RNHX}]$ from Eqn 10 into Eqn 11, the following rate law is obtained:

$$\text{Rate} = \frac{K_1 k_2 [\text{oxidant}]_t [\text{AO8}] [\text{H}^+]}{1 + K_1 [\text{H}^+]} \quad (12)$$

The derived rate law 12 is in good agreement with the experimental results, wherein a first order dependence of rate on each $[\text{oxidant}]_0$ and $[\text{AO8}]_0$ and a fractional-order dependence on $[\text{H}^+]$.

In the present investigations, disparity of dielectric constant of the medium does not have an effect on the rate appreciably. The effect of varying solvent composition and dielectric constant on the rate of reaction has been described in several studies [30-34]. For limiting case of zero angle of approach between two dipoles or an ion-dipole system, Amis [33] has shown that a plot of $\log k'$ versus $1/D$, gives a straight line with a negative slope for a reaction between a negative ion and a dipole or between two dipoles, where a positive slope results for a positive ion-dipole interaction. The total absence of the effect of varying dielectric constant on the rate cannot be explained by the Amis theory [33]. Applying the Born equation, Laidler [34] has anticipated the following equation for a dipole-dipole interaction:

$$\ln k' = \ln k_0 + 3 / 8kT (2/D - 1) [\mu_A^2 / r_A^3 + \mu_B^2 / r_B^3 - \mu_{\neq}^2 / r_{\neq}^3] \quad (13)$$

where k_0 is the rate constant in a medium of infinite dielectric constant, μ represents the dipole moment and r refers to the radii of the reactants and activated complex. It can be seen from Eq. (13) that the rates should be greater in a medium of lower dielectric constant when $r_{\ddagger}^3 = r_A^3 + r_B^3$ representing that the extent of charge scattering in the transition state is different. On the other hand, $r_{\ddagger}^3 \approx r_A^3 + r_B^3$ implies the absence of a dielectric effect of the solvent on the rate, as was observed in the present investigations, signifying that the transition state is not very much different from the reactants with respect to the size and charge of the transition state and the reactants.

Reactions in aqueous medium that are susceptible to acid-base catalysis have been studied in heavy water (D_2O) after equilibrium. Since the majority oxidation reactions of organic compounds involve the cleavage of C-H bond, deuterium isotope effect on such reaction gives information regarding the nature of the rate determining step. In the present investigations, solvent isotope studies have shown that the rate of reaction is higher in D_2O medium. For a reaction involving a fast equilibrium H^+ or OH^- ion transfer, the rate increases in D_2O medium since D_3O^+ or OD^- are a stronger acid and a stronger base respectively, than H_3O^+ and OH^- ions [35-36]. The observed solvent isotope effect of k' (H_2O) and k' (D_2O) < 1 is due to the greater acidity of D_3O^+ compared to H_3O^+ . However, the magnitude of increase in rate in D_2O is small (expected value is 2-3 times greater). This may be due to the fractional order dependence of rate on $[H^+]$. Hence, this observation supports the planned mechanism.

Relative reactivity of CAT and BAT

A comparison of the rates of reaction of CAT and BAT shows that the oxidation of AO8 is about three-fold faster in BAT compared to CAT, under identical set of experimental conditions. This is endorsed by the relative magnitudes of activation energies (Table 2). This trend may be attributed to the difference in electrophilicities of the halocations, Cl^+ and Br^+ ions, involved in the oxidation processes and, is also related to the ease with which these species are generated in reactions. In these oxidation reactions, the electronegativity values of Br^+ and Cl^+ play a vital role. Bromine has the electronegativity of 2.7, while chlorine has a higher value of 2.8. As the electronegativity increases the electropositive nature decreases. Since the halo cations are the reactive species in these oxidation reactions, the electropositive nature is in the order: $Br > Cl$. Therefore the reactivity of BAT is more compared to CAT. This trend may also be due to the moderate difference in the van der Waals's radii of bromine and chlorine. A similar behaviour has been observed in the oxidation of several other substrates using CAT and BAT. The facts furnished in the present research and the literature reports [16, 17, 20, 37-38] lead to conclude that BAT is a stronger oxidant compared to CAT.

The negligible influence of difference of ionic strength and addition of benzenesulfonamide and halide ions are in conformity with the proposed mechanism. The proposed mechanism is also supported by the judicious value of energy of activation and other thermodynamic parameters (Table 2). The fairly high positive values of ΔG^\ddagger and ΔH^\ddagger indicate the transition state is highly solvated while the negative entropy of activation reflects the formation of a compact and ordered transition state. Further, the experimental observation illustrates that there is no effect of benzenesulfonamide, halide ions and ionic strength on the reaction rate which also substantiates the anticipated mechanism.

In the present redox system the optimum conditions for the controlled oxidation of AO8 by CAT and BAT to toluene and 1,2-naphthaquinone in acid medium have been developed. Accordingly, this redox system can be scaled up to industrial operation. Furthermore, AO8 is one of the chief components in the effluents of various industries and is environmentally hazardous and also carcinogenic compound. Hence, the present simple method developed can be adopted for treating the AO8 dye present in industrial effluents to reduce toxicity caused by this dye. Also, this method offers several advantages including short reaction time, cost effective and moderately non-toxic reagents which make the reaction process simple.

IV. Conclusions

The kinetics of oxidation of AO8 by CAT and BAT in acid medium obeys the rate law $-d[\text{oxidant}] / dt = k [\text{oxidant}]_0 [\text{AB}]_0 [\text{H}^+]^x$, where $x = 0.69$ and 0.76 for CAT and BAT respectively. Oxidation products were identified by GC-MS analysis. The present method developed for the oxidative decolorization of AO8 with CAT and BAT is advantageous. Furthermore, the simple and well-designed method developed in the present research can be implemented for treating AO8 present in industrial effluents to diminish the toxicity caused by this dye.

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References

- [1]. Zollinger, H; Colour chemistry: Synthesis, properties and applications of organic dyes and pigments, New York, VCH, 1981
- [2]. Perkowski, J; Ledakowicz, S. *Fibres Text East Eur.* **2002**, 10, 68-72.
- [3]. Waters, B.D.; Colour in Dyehouse Effluent, Cooper, P. Ed. Society of Dyers and Colourists, Bradford, **1995**.
- [4]. Pearce, C.I.; Lloyd, J.R.; Guthrie, J.T. *Dyes Pigments* **2003**, 58, 179-196.
- [5]. Umbuzeiro, G.D.A.; Freeman, H.S.; Warren, S.H.; De Oliveira, D.P.; Terao, Y.;
- [6]. Watanabe, T.; Claxton, L.D. *Chemosphere* **2005**, 60, 55-64.
- [7]. Oakes, J.; Gratton, P. J. *Chem. Soc. Perkin Trans 2* **1998**, 2201-2206. and references therein.
- [8]. Abrahams, E.N.; Dyes and their intermediates, London, UK Edward Arnold Ltd. 1977.
- [9]. Ligrini, O.; Oliveros, E. Braun, A. *Chem Rev* **1993**, 93, 671-698.
- [10]. Roxon, J.J.; Ryan, A.J.; Wright, S.E.; *Food Cosmet Toxicol* **1967**, 5, 367-369.
- [11]. J.P. Shubha, Puttaswamy, Euro. J. Chem. 3(1), 2012, 112-118
- [12]. Puttaswamy, J.P. Shubha, R.V. Jagadeesh, *Transition Metal Chemistry* (2007) 32:991-999
- [13]. Jennings VJ, *Critical Rev Anal-Chem.* 1974: 407-419.
- [14]. Campbell MM, Johnson G. *Chem Rev.* 1978: 78: 65-79.
- [15]. Banerji KK, Jayaram B & Mahadevappa D S, *J Sci Ind Res.* 1987:46: 65-76.
- [16]. Kolvari E, Ghorbani-Choghmarani A, Salehi P, Shirini F, Zolfigol MA. *J Iran Chem Soc.* 2007: 4(2):126-174.
- [17]. Rangappa KS. *J Indian Chem Soc.* 2004:81:1025-1037.
- [18]. Naidu HMK, Yamuna B, Mahadevappa DS. *Indian J Chem.* 1987:26A:114-117.
- [19]. Rangappa KS, Ramachandra H, Mahadevappa DS, Gowda NMM. *Int J Chem Kinet.* 1996:28:265-274.
- [20]. Puttaswamy, Jagadeesh R.V. *Int J Chem Kinet.* 2006:38:48-56.
- [21]. David Williams A, Thomas Lenke L. *Foye's Principles of Medicinal Chemistry.* Lippincott Williams and Wilkins. 2005:751-790.
- [22]. Bertram G Katzung. *Basic and Clinical Pharmacology.* McGraw-Hill, 2006:574-576.
- [23]. Castillo MA, Bruzzone L. *Analytical Sci.* 2006:22:431-433.
- [24]. Roskar R, Kmetec V. *J Chromatogr B.* 2003:788:57-64.
- [25]. Sein MM, Zedda M, Tuerk J, Schmidt TC, Golloch A, Sonntag CV. *Environ Sci Technol.* 2008:42:6656-6662.
- [26]. Perez-Estrada, LA, Malato S, Gernjak W, Aguera A, Thurman EM, Ferrer I, Fernandez-Alba AR. *Environ Sci Technol.* 2005:39:8300-8306.
- [27]. Morris J C, Salazar JA, *J Am Chem Soc.* 1948:70:2036-2041.
- [28]. Nair CGR, Lalithakumari R, Indrasenan P. *Bromamine-T as a new oxidimetric titrant.* *Talanta.* 1978:25:525-527.
- [29]. Hardy FF, Johnston JP, *J Chem Soc. Perkin Trans II.* 1973:742-750.
- [30]. Bishop E, Jennings VJ. *Talanta.* 1958:1:197-199.
- [31]. Murthy ARV, Rao BS. *Proc Indian Acad Sci.* 1952:35:69-72.
- [32]. Pryde BG, Soper FD. *J Chem Soc.* 1931:1510-1512.
- [33]. Higuchi T, Hasegawa T. *J Phys Chem.* 1965:69:796-799.
- [34]. House JE. *Principles of Chemical Kinetics.* Academic press. 2007:102-107.
- [35]. Moelwyn-Hughes EA. *The kinetics of reaction in solutions,* Oxford, Clarendon Press, 1947: 374-381.
- [36]. Frost AA, Pearson RG, *Kinetics and Mechanism,* New York, Wiley, 1961:135-149.
- [37]. Amis ES. *Rates Mechanisms and Solvent.* *Anal Chem.* 1955:27:1672-1679.
- [38]. Laidler KJ. *Chemical kinetics.* New Delhi, Tata Mc Graw-Hill, 1995:211-228.
- [39]. Reichardt C. *Solvent and Solvent Effects in Organic Chemistry,* New York, Wiley-Vctt, 2003:219-237.
- [40]. Collins CJ, Bowman NS. *Isotope Effects in Chemical Reactions,* New York, Van-Nostrand 1970:267.
- [41]. Kohen A, Limbach HH. *Isotope Effects in Chemistry and Biology.* Florida, CRC Press., 2006:827-844.
- [42]. Puttaswamy, Mahadevappa DS, Rangappa KS. *Bull Chem Soc Jpn.* 1989:62:3343-3348.
- [43]. Puttaswamy, Shubha, J.P. *AICHE,* **2009**, 55(12), 3234-3240.

Table 1. Effect of Variation of oxidant, AO 8 and HClO₄ concentrations on the reaction rate at 298 K.

10 ³ [oxidant] ₀ (mol dm ⁻³)	10 ⁴ [AO 8] ₀ (mol dm ⁻³)	10 ⁴ [HClO ₄] (mol dm ⁻³)	10 ⁴ k' (s ⁻¹)	
			CAT	BAT
0.5	2.0	2.0	2.12	2.35
1.0	2.0	2.0	3.05	5.12
2.0	2.0	2.0	7.20	10.8
4.0	2.0	2.0	13.8	18.5
5.0	2.0	2.0	16.3	23.2
2.0	2.0	0.5	3.24	6.12
2.0	2.0	1.0	5.28	8.54
2.0	2.0	2.0	7.20	10.8
2.0	2.0	4.0	9.35	12.6
2.0	2.0	5.0	12.6	15.2
2.0	0.5	2.0	7.32	10.5
2.0	1.0	2.0	7.15	10.0
2.0	2.0	2.0	7.20	10.8
2.0	4.0	2.0	7.11	11.2
2.0	5.0	2.0	7.36	10.2

Table 2. Temperature dependence on the reaction rate and activation parameters for the oxidative decolorization of AO8 by CAT and BAT in acid medium

Temperature (K)	$10^4 k / (s^{-1})$	
	CAT	BAT
283	4.35	5.16
288	5.05	6.52
298	7.20	10.8
308	9.75	14.7
313	12.6	16.5
E_a (kJ mol ⁻¹)	25.0	29.2
ΔH^\ddagger (kJ mol ⁻¹)	22.8	26.7
ΔG^\ddagger (kJ mol ⁻¹)	91.1	90.3
ΔS^\ddagger (JK ⁻¹ mol ⁻¹)	-229	-214
Log A	7.34	7.48

[oxidant]₀ = 2.0 x 10⁻³ mol dm⁻³; [AO8]₀ = 2.0 x 10⁻⁴ mol dm⁻³; [HClO₄] = 2.0 x 10⁻³ mol dm⁻³.

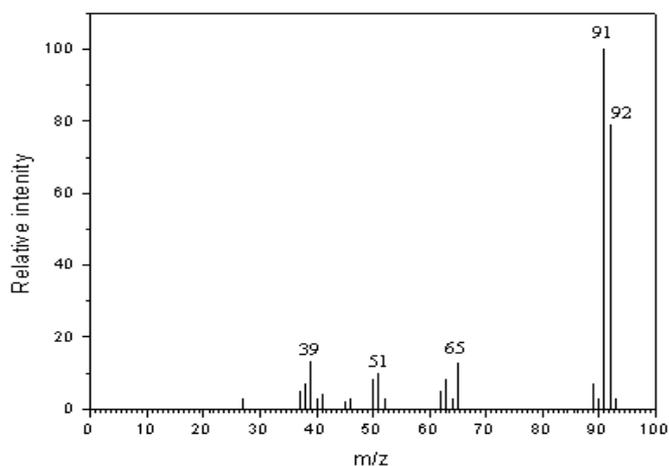


Fig. 1 GC-Mass spectrum of toluene with its molecular ion peak at 92 amu.

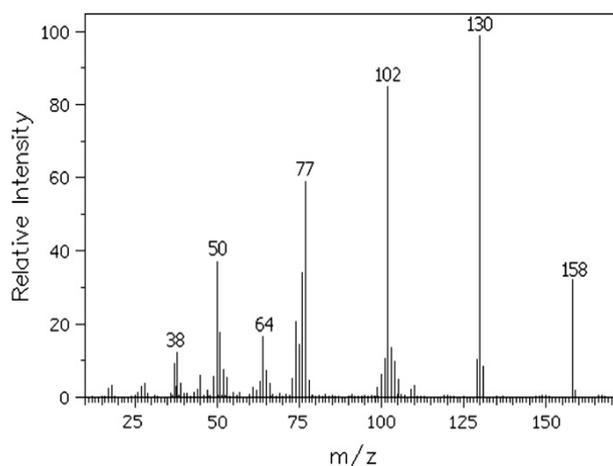


Fig. 2 GC-Mass spectrum of naphthaquinone with its molecular ion peak at 158 amu.

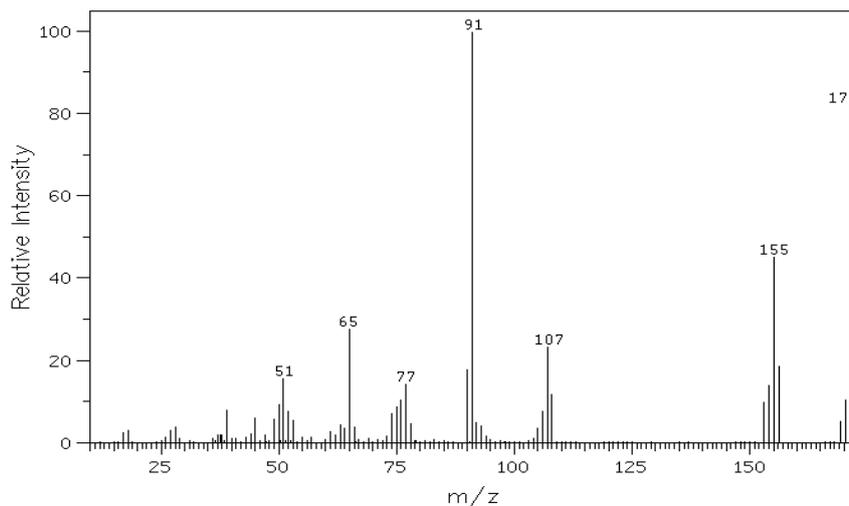


Fig. 3 GC-Mass spectrum of p-toluenesulfonamide with its molecular ion peak at 171 amu.

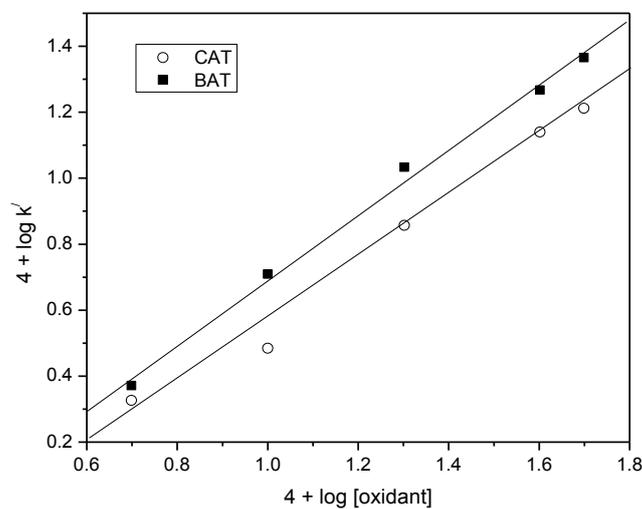


Fig. 4 Plot of log [oxidant] versus log k' .

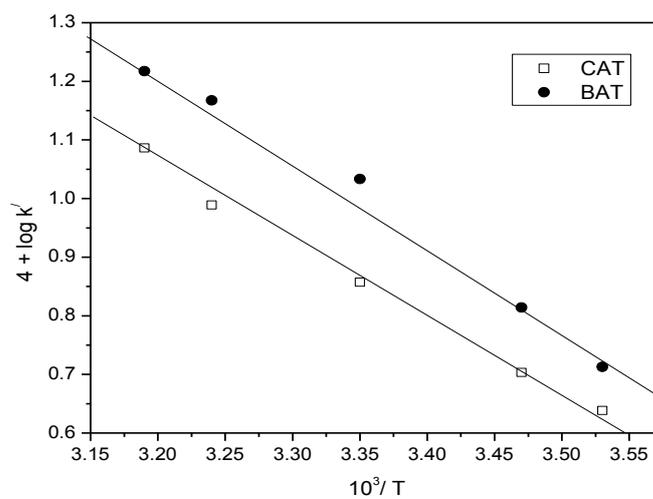
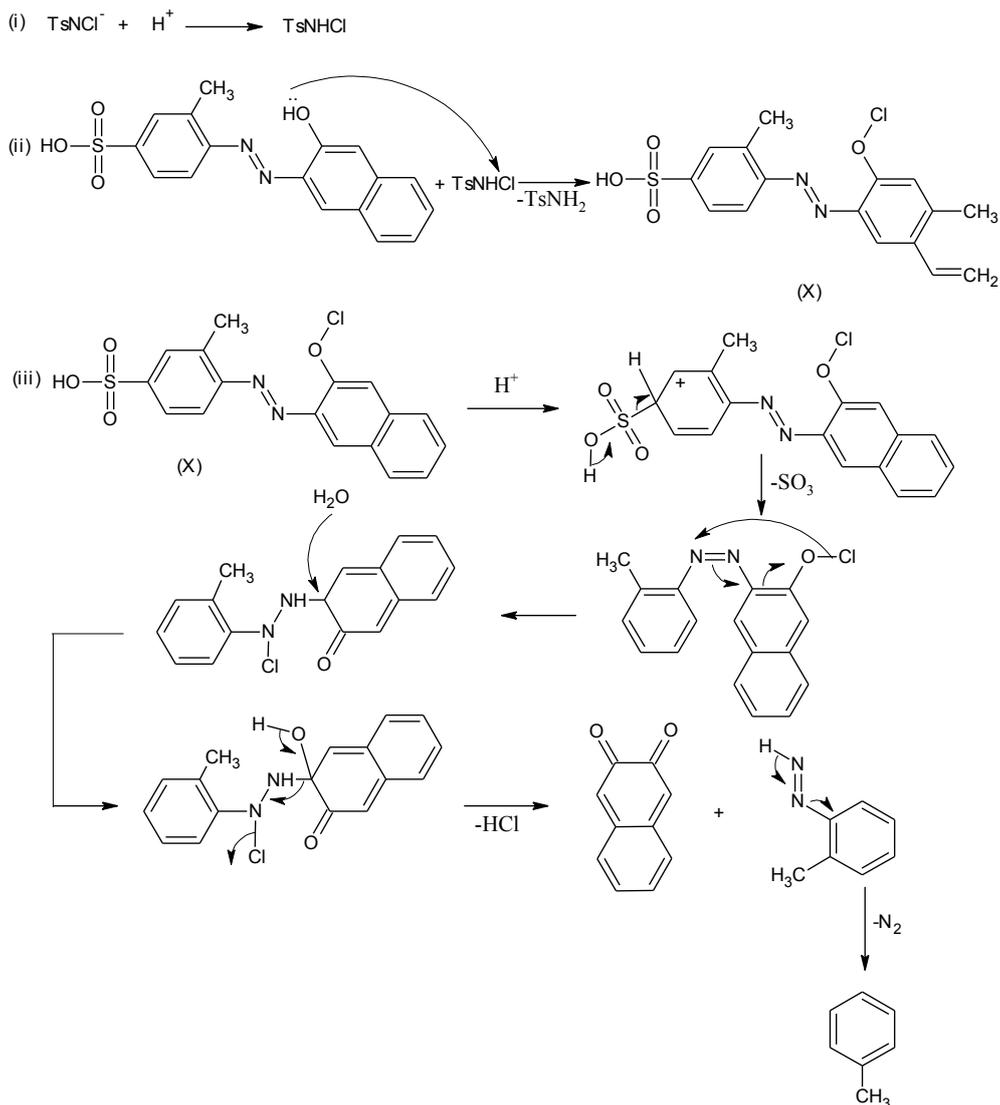


Fig. 5 Plot of 1/T versus log k' .



Scheme 2. Detailed mechanistic interpretation for the oxidation of AO8 by CAT and BAT in acid medium.